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EXECUTIVE SUMMARY

DIFFUSION OF RADIONUCLIDES IN NON-METALLIC SOLIDS OF DIFFERENT SHAPES. PART II- MODEL VALIDATION

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Empirical and semi-empirical relations are widely used to interpret radionuclide leaching from solid waste forms. Although these relations provide a reasonable fit for the data, they cannot be used to transpose the data to other experimental configurations (i.e. scale up), or to extrapolate the results to longer times. A set of rigorous model equations for the release of radionuclides from non-metallic solids of different shapes was developed and presented in a separate report (Part I). These model equations were obtained by solving the diffusion equation which includes a first order chemical reaction term and/or the radionuclide activity decay. Leaching experiments were carried out to test the validity of the model equation developed for finite cylinders. Good agreement was obtained between the cumulative fractional release of tritiated water predicted by the model and observed experimentally. The model was further tested with literature data and was found to provide a better representation than previously achieved. Extrapolation of experimental results to longer times and application to field configurations can now be undertaken with greater confidence.

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740632-530-050	837.822	July 10, 1986	86-55-K

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To: Dr. D. Mills
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DIFFUSION OF RADIONUCLIDES IN NON-METALLIC SOLIDS OF DIFFERENT SHAPES. PART II- MODEL VALIDATION

L.A. Gonzalez and J.M. Braun

Leaching experiments from cylindrical solid waste forms were carried out to test the validity of the model equation for finite cylinders developed in an earlier report (Part I). Experimental and literature data were used to demonstrate that a better representation of radionuclide leaching data was obtained when using the present model for finite cylinders.

1.0 INTRODUCTION

Handling, storage and safe disposal of low and medium level radioactive materials from nuclear generation plants require a good understanding of the interaction of these potentially hazardous compounds and the non-metallic solids in which they are usually contained or come in contact with. Low and medium level radioactive contaminated liquid wastes can be immobilized in solid matrices using different fixing media. These solid matrices can then be placed in protective repositories. In order to determine the possible impact of these repositories on the environment, it is necessary to determine the release rate of the radionuclides from the waste forms.

Several mathematical treatments have been used to characterize the leaching behavior of radionuclides from different solid waste forms. Although empirical relations provide a reasonable fit for the data /1/, they cannot be used to transpose the results to more realistic experimental conditions (i.e. scale up to field conditions) or to extrapolate the data to longer times.

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The semi-infinite slab model has often been used to interpret leaching data from solid waste forms regardless of the shape of the solid /2-4/. The deviations of the predicted values from the experimental data led to the development of more complex models/5-7/. These models, however, can require greater computer capabilities and often have not been validated with existing experimental data/6,7/.

Rigorous yet tractable model equations describing the interaction of radionuclides with non-metallic solids of different shapes were developed and presented as Part I in a separate report/8/. The second objective of this project, which is presented in this report, was to test the validity of the model equations with the commonly used finite cylinder configuration. Leaching data for tritiated water as well as literature data obtained on other radionuclides were used for that purpose.

2.0 MODEL EQUATIONS

The model equations describing the interaction of radionuclides with cylindrical solid waste forms were discussed extensively in Part I/8/. For the cumulative fractional release ($\Sigma An/Ao$) one has

$$\frac{\Sigma An}{Ao}\frac{V}{S} = 32\,\frac{1\ D}{\pi^2 a(2l+a)}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{\beta_{m,n}}{\alpha_m^2(2n+1)^2} \qquad (1)$$

$$\times\ \frac{[Kt(K+D\beta_{m,n})+D\beta_{m,n}(1-\exp[-t(K+D\beta_{m,n})])]}{(K+D\beta_{m,n})^2}$$

where V/S is the volume to surface ratio, 2l and a the height and radius of the cylinder, K and D the reaction rate constant and the diffusivity of the radionuclide in the solid matrix, with α_m the roots of the Bessel function of zero order, and

$$\beta_{m,n} = \alpha_m^2 + (2n+1)^2\pi^2/(4\ l^2)$$

Expansion of the double series in equation 1 considering only the first term in n and the first two terms in m gives

$$\frac{\Sigma An}{Ao}\frac{V}{S} = 32\,\frac{1}{\pi^2 a(2l+a)}\left\{DKt\left[\frac{\beta_{1\emptyset}}{K+D\beta_{1\emptyset}} + \frac{\beta_{2\emptyset}}{K+D\beta_{2\emptyset}}\right]\right. \qquad (2)$$

$$\left. + \frac{D^2\beta_{1\emptyset}^2(1-\exp[-t(K+D\beta_{1\emptyset})])}{\alpha_1^2(K+D\beta_{1\emptyset})^2} + \frac{D^2\beta_{2\emptyset}^2(1-\exp[-t(K+D\beta_{2\emptyset})])}{\alpha_2^2(K+D\beta_{2\emptyset})^2}\right\}$$

Equation 2 can be used to analyze the experimental leaching data of radionuclides from cylindrical solid waste forms containing an initial uniform concentration.

In order to determine the validity of and improvement achieved with equation 2, the results obtained by fitting the experimental data to this equation can be compared to those obtained by applying the semi-infinite slab model to the same data. The semi-infinite slab model without chemical reaction has the form/9/

$$\frac{\sum An}{Ao} \frac{V}{S} = 2\ (D/\pi)1/2\ t1/2 \qquad (3)$$

3.0 EXPERIMENTAL

Tritiated water (30 μCi/mL) was immobilized in Portland Cement (PC) and Water Extendible Polyester (WEP) waste forms using the same solid/water ratios as Hawthorne/10/. The water content of the cement specimens was 0.22 g water/g product, and 0.50 g water/g product for the WEP samples. Cylinders of different sizes (2 x 2, 4 x 2, 3 x 3 and 6 x 6 for length and diameter in cm) were prepared with these two mixtures. After solidifying and curing, the cylindrical samples were placed in sealed plastic containers. Five volumes of distilled water were added to each container. The tritiated water leachate was monitored by liquid scintillation counting.

The cumulative fractional release of radionuclides , corrected for volume to surface ratio (V/S), was fitted to equation 2 to obtain the diffusivity and the reaction rate constant for each sample size. The data were also fitted to the semi-infinite slab model for comparison purposes. Analysis of the data was performed on a personal microcomputer (Compaq Deskpro) using a special equation fitting program, "Fit All" (MTR Software, Toronto, Ontario). The main feature of this software package is that one can define a non-linear model equation (such as equation 2) in terms of its unknown parameters (K and D). With initial guess values for these parameters an iteration process is started. The cycle is completed either when a set number of iterations is reached or when the difference between two consecutive variances is lower than a predetermined value.

4.0 RESULTS AND DISCUSSION

The experimental results for the cumulative fractional release of tritiated water from cylindrical waste forms of Portland cement and water extendible polyester are presented in this section. Analysis of leaching data for other radionuclides gathered from the literature is also presented.

4.1 EXPERIMENTAL RESULTS

Results for the cumulative fractional release of tritiated water from a 2x2 cement cylindrical waste form are plotted as a function of time in Figure 1. The solid line represents the best fit of the data according to our model, while the dashed line represents the same data fitted to equation 3. As can be seen a considerable improvement in the fit of the experimental data is obtained using the finite cylinder model. At long times equation 3 leads to a drastic overestimate of the radionuclide release from the waste form while the curve for equation 2 remains extremely close to the experimental results extending to nearly 200 days. It is quite obvious that a much more realistic and credible extrapolation of the experimental results can be obtained with the finite cylinder model.

Diffusivity and rate constant are two parameters of equation 2 and these can, in turn, be calculated from the experimental data. The diffusivity, which represents the mobility of the radionuclide in the matrix, was 6.8×10^{-8} cm^2 s^{-1} for the data of Figure 1. The rate constant, which represents a combination of the radioactivity decay rate and the dissolution rate, was 1.5×10^{-8} s^{-1} for the same data. It should be noted in particular that the magnitude of these parameters is commensurate with the results obtained in other mass transport studies/11/ with diffusivities of the order of 10^{-8} $cm^2 s^{-1}$. Diffusivities and rate constants obtained for all cement sample sizes are listed in Table I.

As can also be seen in Table I and as is commonly the case, the diffusivity of tritiated water in the cement matrix is a function of specimen size (in this instance, surface to volume ratio). A similar dependence of the diffusivity on the specimen size of a resin/cement matrix was observed in the leaching results reported for cesium-137 by other researchers/4/. This dependence may be due to a number of causes including differences in the

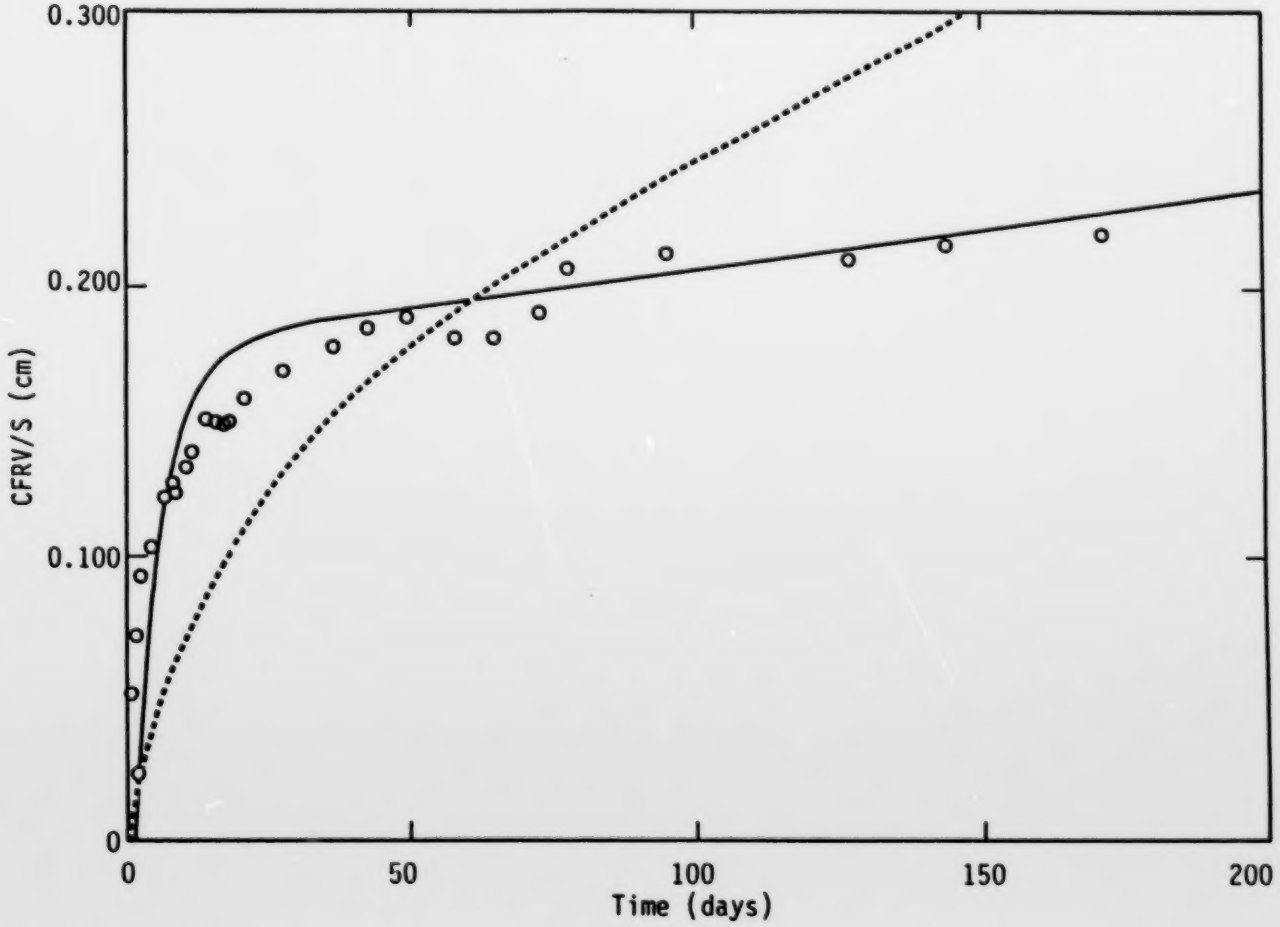

Figure 1

Tritiated water release from 2 x 2 cement cylindrical waste form (—finite cylinder model, ... semi-infinite slab equation).

pore structure of the different size samples and/or to a concentration dependent diffusivity.

The value for the rate constant, as seen in Table I, was essentially constant for the different samples sizes, except for the largest specimens whose values were negative. These negative values indicate that over the leaching period considered (200 days), the radionuclide release is controlled only by diffusion rather than by a combination of diffusion and dissolution rates (diffusivity and rate constant are of the same order of magnitude). Similar results were obtained with the WEP samples as can be seen in Table II, with however somewhat lower diffusivity and rate constant.

4.2 Sample Size Effect

The effect of sample size on the release rate of radionuclide from the waste form is an important factor in leaching studies since results obtained with small laboratory scale samples are used to estimate the release rates from a full size (200 liter) specimen. Under conditions where the diffusivity, rate constant and porosity of the sample remain unchanged, the release rate from specimens of different sizes is affected only by the variation of the surface to volume ratio. Application of the semi-infinite slab model gives a simple relationship between surface to volume ratio and release rates of radionuclides from solid waste forms of different sizes/9/.

Variation of the diffusivity with sample size however implies that release rates obtained from waste forms of different sizes are no longer directly proportional to their surface to volume ratios. Therefore a new relationship has to be found in order to estimate radionuclide releases from full size specimens.

Concentration dependent diffusivities have often been found to obey an exponential equation of the form

$$D=Do\ \exp(A\ [S/V]) \qquad (4)$$

where Do and A are constant. Fitting the data from Tables I and II gave the values of 6.3×10^{-10} and 8.0×10^{-10} $cm^2 s^{-1}$ for Do in the case of cement and WEP samples and 1.30 and 0.34 cm for A for the same samples respectively.

This new relationship between diffusivity of the radionuclide and

Table I

Mass Transport Parameters for Tritiated Water in Cement

Half Length	Radius	Initial Release	Diffusivity	Rate/Decay Constant
l (cm)	a (cm)	$R_o \times 10$ (cm)	$D \times 10^9$ ($cm^2 s^{-1}$)	$K \times 10^8$ (s^{-1})
1	1	-0.35	68.0	1.5
1	1	-0.37	72.0	1.6
2	1	0.76	4.9	1.9
2	1	0.73	5.4	1.7
1.5	1.5	0.84	10.0	1.4
1.5	1.5	0.89	9.3	1.7
3	3	1.1	2.9	< 0
3	3	1.1	2.9	< 0

Table II

Mass Transport Parameters for Tritiated Water in WEP

Half Length	Radius	Initial Release	Diffusivity	Rate/Decay Constant
l (cm)	a (cm)	$R_o \times 10$ (cm)	$D \times 10^9$ ($cm^2 s^{-1}$)	$K \times 10^8$ (s^{-1})
1	1	0.18	2.4	1.6
2	1	0.18	1.1	1.3
2	1	0.17	1.1	1.3
1.5	1.5	0.22	2.4	1.2
1.5	1.5	0.21	2.3	1.2
3	3	0.18	0.7	< 0
3	3	0.18	0.7	< 0

sample size must now be introduced into equation 1 to derive a new relation for cumulative releases from specimens of different sizes. In certain cases and as done here for equation 2 higher terms in this equation can be neglected to simplify the relationship.

4.3 LITERATURE DATA

The finite cylinder model was further tested with leaching data obtained by other investigators. Leaching data/10/ for tritiated water in a 5x5 cement cylindrical waste form are plotted as a function of time in Figure 2. As before the solid line corresponds to the fit obtained with our finite cylinder model, while the dashed line represents the semi-infinite model equation. Again a much improved representation of the data is obtained when using the finite model. Moreover extrapolation to longer times indicates that predictions based on the semi-infinite model equation would be increasingly overestimated. It should also be noted that a better fit of the data would have been obtained had more experimental points been collected in this study.

A comparison between the two representations for the release of Cs-137 from a 10x5 resin/cement solid cylinder reported by Dayal/4/ is shown in Figure 3. Although no significant difference is observed between the finite cylinder model (solid line) and the semi-infinite model (dashed line) at short times, the extrapolation of the results based on the finite cylinder model seems to be more appropriate. While the extrapolation by our equation levels off suggesting an equilibrium state between the radionuclide in the waste and in the surrounding fluid, the extrapolation by the semi-infinite model goes through the theoretical maximum value of 1 for the cumulative fractional release.

The literature data for Cs-137 leaching from cylindrical phosphate/glass composites/2/ are shown in Figure 4. As before the solid line represents the finite cylinder model and the dashed line the semi-infinite model. As can be observed in this Figure the release from this waste form is very slow reflecting the low diffusivity of this radionuclide in this matrix(1.9×10^{-13} $cm^2 s^{-1}$). The closeness of the predicted values by the finite cylinder model to the experimental data clearly demonstrate the better representation obtained with our model than with the semi-infinite equation. Since a better representation of the leaching

data from cylindrical waste forms is obtained when using the model developed for finite cylinders, it is expected that this model would also give a more accurate extrapolated value of the cumulative fractional release of radionuclides at longer times.

4.4 GENERAL APPLICATION OF MODEL EQUATIONS

Equation 1 can be applied to experimental leaching data from cylindrical waste forms in a number of ways. As demonstrated in this study, expansion of the summation considering only the first two terms yields equation 2. The application of equation 2 proved to be adequate to represent experimental and literature leaching data of radionuclides from solid cylindrical waste forms.

To obtain greater accuracy of the fitted values, more terms of the series in equation 1 must be added to equation 2. As in the case of the finite cylinder model, the equations for other geometries can also be expanded in a similar fashion. Comparable results would be expected.

5.0 CONCLUSIONS

The finite cylinder model equations developed in the present study for analyzing the release of radionuclides from solid waste forms were validated with experimental and literature leaching data. Comparison with the commonly used semi-infinite model showed that an improved fit of the data was achieved with the finite cylinder model. The diffusivities, which appear as parameters of the model equations, were found to be of the same order of magnitude as those commonly determined in mass transport studies.

The model provides a superior fit of the results at short times and it can be anticipated that the finite cylinder model will afford greater confidence in the extrapolation of the cumulative fractional release of radionuclides to longer times. Similar results are also expected for the models developed for other geometries (sphere, rectangular block, composite cylinder, semi-permeable and composite slabs) as described in detail in Part I.

It was also established that for both cement and WEP matrices diffusivity of the radionuclide was a function of specimen size. The variation of radionuclide diffusivity with sample size invalidates the commonly used linear relationship between cumulative

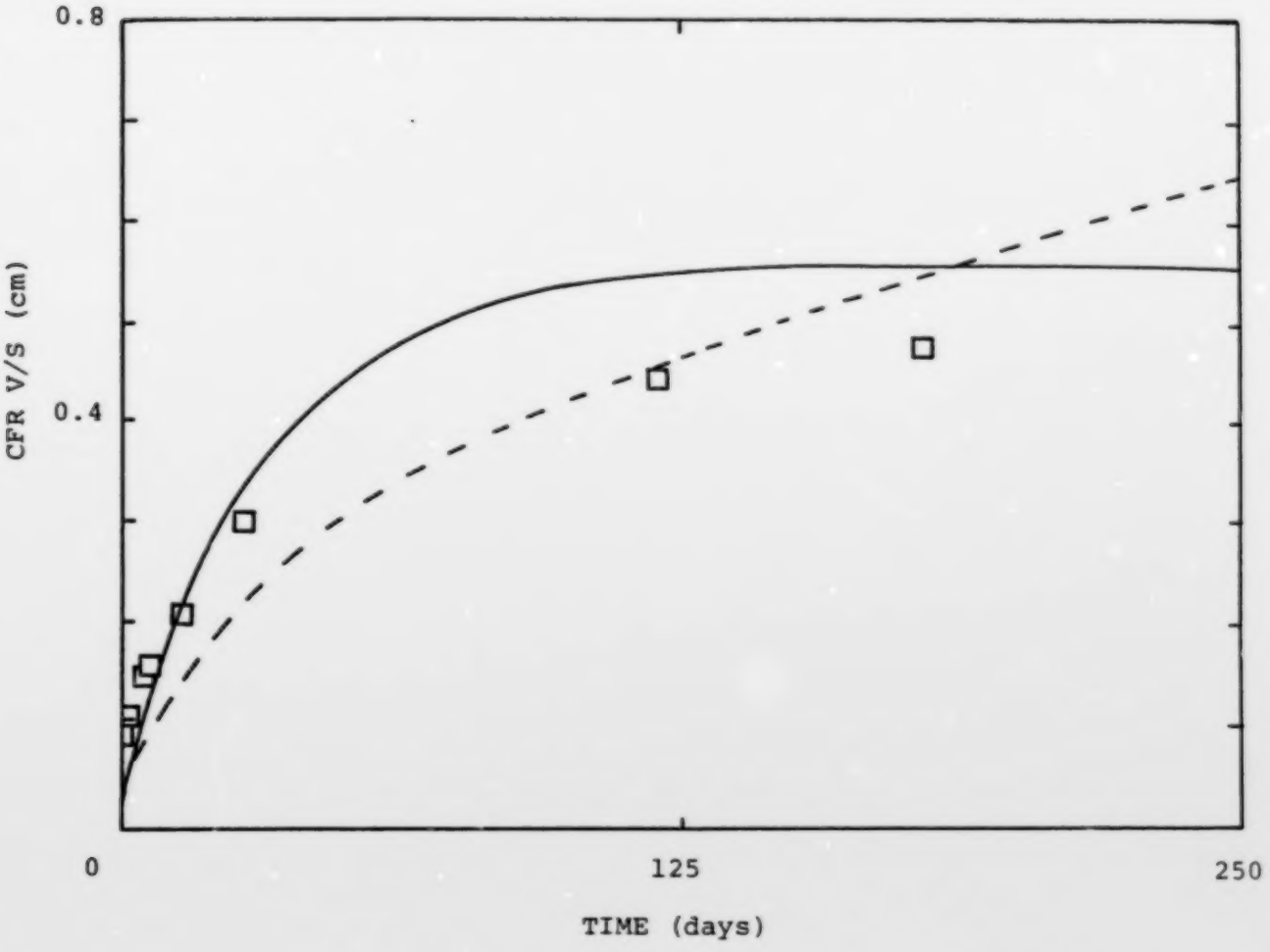

Figure 2

Tritiated water release from 5 x 5 cement cylindrical waste form(—finite cylinder model, ... semi-infinite slab equation, literature data/10/).

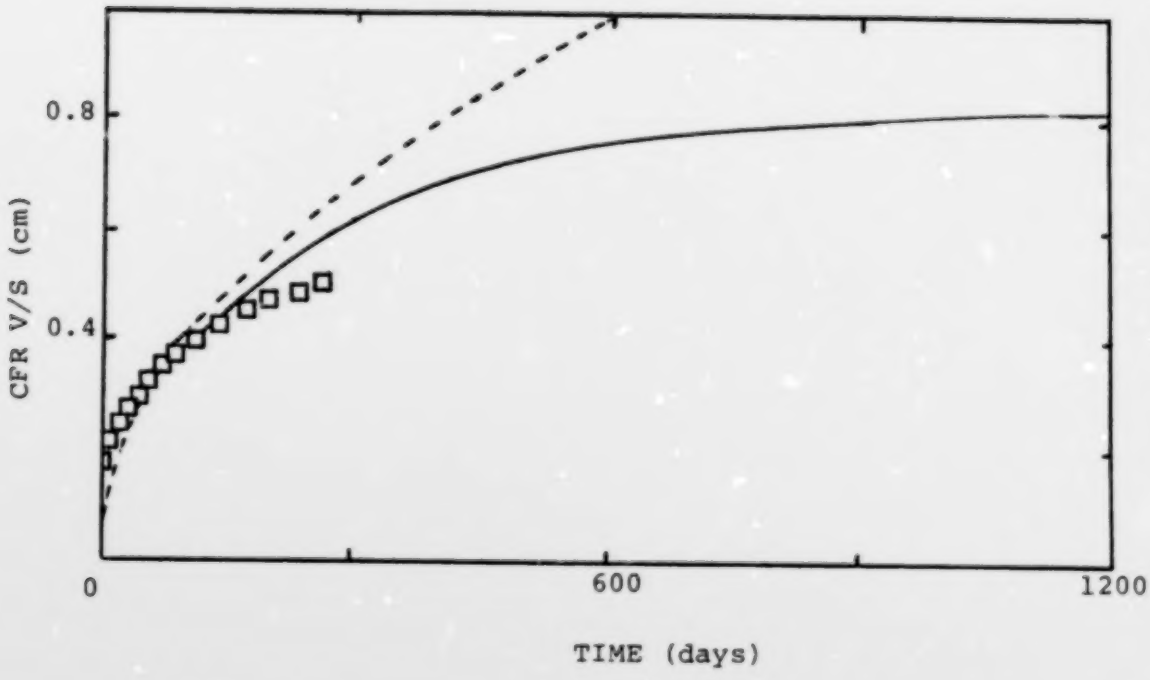

Figure 3

Cesium-137 release from 10 x 5 resin/cement cylindrical waste from(—finite cylinder model, ---- Semi-infinite slab equation, literature data/4/).

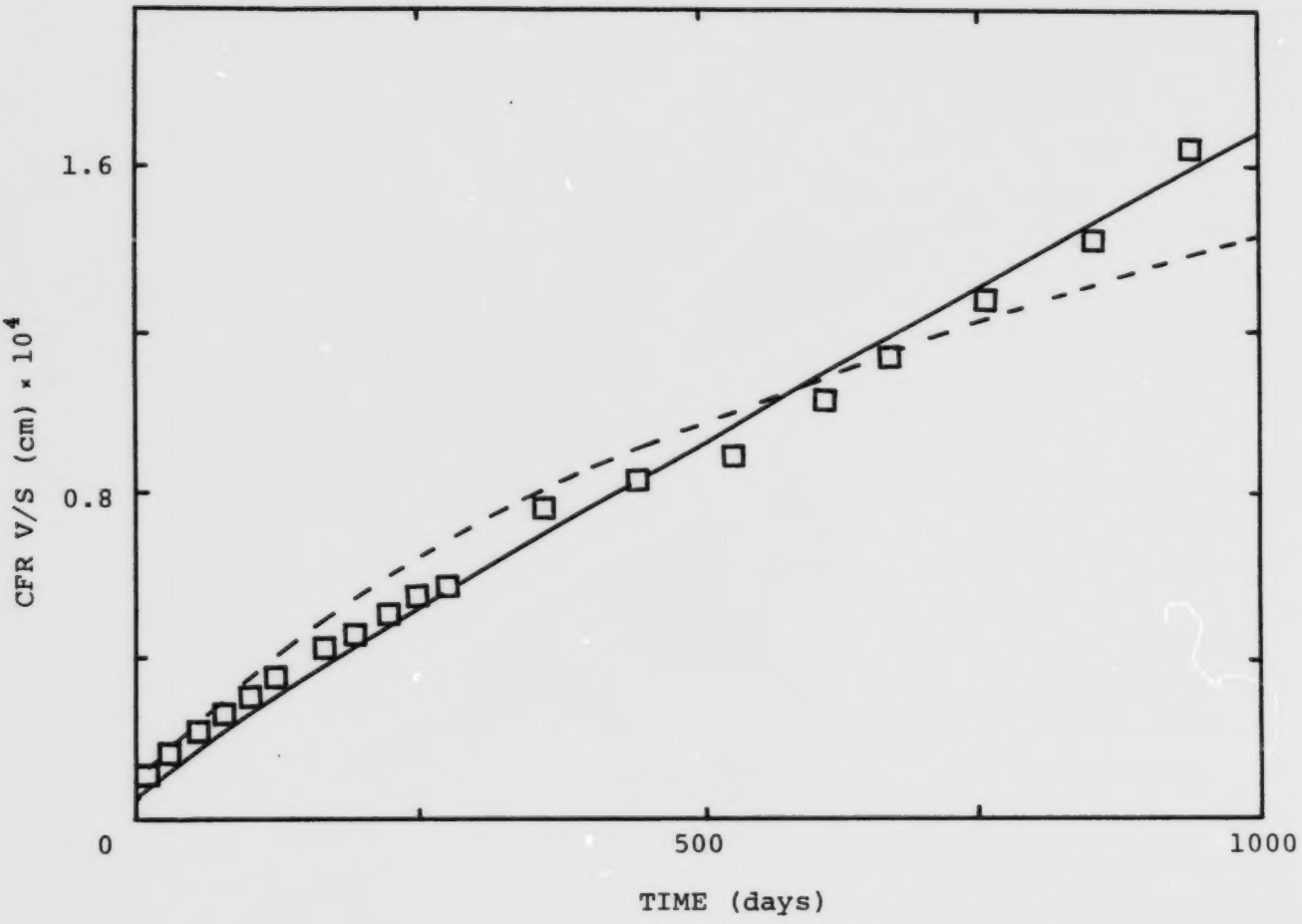

Figure 4

Cesium-137 release from 5 x 5 phosphate/glass cylindrical waste form(—finite cylinder model, ... semi-infinite slab equation, literature data/9/).

fractional release and specimen surface to volume ratio. Based on the experimental results obtained a more realistic equation can be developed. Such equation can be used to estimate the radionuclide release from cylindrical waste forms of larger sizes. However this equation may not be generally applicable to all radionuclides and wastes and detailed data analysis would be required for individual cases.

In spite of their apparent mathematical complexity, the model equations can be easily fitted to experimental data with limited computing and software requirements. The ease of use and accuracy of the model developed for interpreting radionuclide releases from cylindrical waste forms and other geometries provide an important tool in the analysis of the interaction between radionuclides and non-metallic solids.

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